

## 6.—THE OCCURRENCE OF RUBIDIUM, CAESIUM AND THALLIUM IN SOME WESTERN AUSTRALIAN MICAS.

By D. G. MURRAY, A.A.C.I., and F. E. CHAPMAN, A.A.C.I.

*Read 12th May, 1931; Published 25th June, 1931.*

The metals, caesium and rubidium are classed as the rarer alkali metals and are commonly found associated with the more familiar elements sodium and potassium in certain members of the mica group of minerals. Lepidolite mica which also contains considerable amounts of another alkali metal, lithium, is the main known rubidium bearing mineral, containing from traces up to 3 per cent. of rubidium oxide, and from traces up to 1 per cent. of caesium oxide also. Thallium also occurs in very small quantities in certain micas

Lepidolite has been found in a large number of places in Western Australia, and as its suitability as a prospective source of caesium and rubidium would depend on the quantity of these metals present the determination of these constituents is one of economic as well as scientific importance. As the occurrence of these three metals had not previously been recorded in any Western Australian micas, spectroscopic examinations of three samples of mica from different localities in the State were carried out by one of us (F.E.C.) in order to establish their presence or otherwise. The result of his work was to definitely establish the presence of all three elements in two of the minerals examined. It might be mentioned in passing that caesium had also been detected spectroscopically by the same worker in the rare caesium bearing variety of beryl, roosterite, found in a lithium bearing pegmatite at Wodgina, Western Australia. In the preparation of the samples for spectroscopic examination chemical methods were employed to separate as far as possible the caesium, rubidium and thallium from the other constituents of the micas. For the detection of caesium and rubidium a solution of what was assumed to be the chlorides of these metals was obtained and examined by the visual spectroscope. The thallium was separated as sulphide and this precipitate tested in a similar manner.

The results were:—

Mica.	Quantity taken.	Rubidium.	Caesium.	Thallium.
Lepidolite mica, Tappa Tappa	1 gm.	Present	Present	Present
Lepidolite, Londonderry ...	1 gm.	Present	Present	Present
Lepidolite, Widgiemooltha District	1 gm.	Absent	Absent	Present

A permanent spectrogram record of the presence of rubidium, caesium and thallium in the mica from Londonderry was also obtained by means of a quartz spectrograph, pure salts of rubidium and caesium being used to make standard exposures with for confirming the lines obtained from the mica.

An attempt was then made to roughly estimate the quantity of rubidium and caesium present in standard solutions of varying strengths by comparing the intensity of the lines. This method was found to be unsatisfactory, due to the limited range of intensities of rubidium lines and the error due to eye fatigue. A detailed description of the methods is given in a later paragraph.

The presence of the three elements having been established in two micas by means of the spectroscope, quantitative analyses were made of a number of micas from various parts of the State in order to determine if possible the actual quantities of these constituents present. The chemical characteristics of caesium and rubidium are very similar to those of potassium, and failure to separate them during the course of the determination of the alkali metals would result in a serious error in the potash figure.

Detailed descriptions and analyses\* of several of the micas selected for the determination of caesium, rubidium and thallium have already been published, but no attempt had been previously made to determine the percentage of these constituents present. The results obtained were:—

			Lepidolite Londonderry (Uniaxial).	Lepidolite Londonderry (Biaxial).	Lepidolite Poona.	Lepidolite Ubini.
			%	%	%	%
Li <sub>2</sub> O	...	...	5·89	5·56	4·92	4·00
Na <sub>2</sub> O	...	...	·84	·62	·86	·36
K <sub>2</sub> O	...	...	10·03	10·10	9·24	10·55
Rb <sub>2</sub> O	...	...	1·41	2·02	1·72	1·10
Cs <sub>2</sub> O	...	...	trace†	trace	trace	trace
Tl	...	...	trace	trace	trace	trace

  

			Lepidolite Tabba.	Lepidolite Ravensthorpe.	Lepidolite Wodgina.	Zinnwaldite Ubini.
			%	%	%	%
Li <sub>2</sub> O	...	...	3·24	3·32	3·18	1·13
Na <sub>2</sub> O	...	...	·92	·46	·56	·19
K <sub>2</sub> O	...	...	10·34	9·52	9·64	9·76
Rb <sub>2</sub> O	...	...	1·12	2·34	1·46	·46
Cs <sub>2</sub> O	...	...	·25	trace	trace	trace
Tl	...	...	trace	trace	trace	trace

\* Journal of the Royal Society, W.A., Vol. 13; Journal Natural History and Science Society, W.A., Vol. 4.

† Under 0·05 per cent.

The following alkali determinations in some micas from other parts of the world are given for comparison with the above.

	Lepidolite Nagaton Japan.	Lepidolite Maine, U.S.A.	Lepidolite Maine, U.S.A.	Zinnwal- dite Tanokami Japan.	Lepidolite Nubeb, S.W. Africa.
	%	%	%	%	%
Li <sub>2</sub> O ... ..	2.49	4.34	3.87	4.24	4.93
Na <sub>2</sub> O ... ..	3.20	2.17	.13	5.00	2.15
K <sub>2</sub> O ... ..	9.13	8.03	8.82	7.89	9.26
Rb <sub>2</sub> O ... ..	.96	2.44	3.73	.81	1.73
Cs <sub>2</sub> O ... ..	...	.72	.08	...	.60

### METHODS OF ANALYSIS.

The following method of analysis was employed for the determination of the metals of the alkali group.

Using the Lawrence Smith method for alkalis a weight of total mixed chlorides of the alkali group was obtained. The weighed chlorides were treated with a mixture of absolute alcohol and concentrated hydrochloric acid which gave a precipitate of sodium and potassium chlorides and a solution containing lithium, rubidium and caesium. The solution was evaporated to dryness on the water bath and retreated with the alcohol hydrochloric mixture. Any further precipitate of sodium and potassium chloride was added to the main precipitate, the whole dissolved in water and evaporated to dryness with a drop or two of hydrochloric acid, gently ignited and weighed as the mixed chlorides of sodium and potassium. The potassium was separated and weighed in the usual manner as chloroplatinate.

The filtrate containing the lithium, rubidium and caesium was evaporated to dryness and the mixed chlorides gently ignited and weighed. The chlorides were dissolved in water and the rubidium and caesium separated and weighed as chloroplatinates. This precipitate was dissolved in hot water containing a few drops of hydrochloric acid and the solution saturated with H<sub>2</sub>S. The platinum sulphide was filtered off, the filtrate containing the rubidium and caesium evaporated to dryness and the chlorides of rubidium and caesium ignited and weighed. This weight was deducted from the weight of mixed rubidium, caesium and lithium chlorides to obtain the weight of lithium chloride. The rubidium and caesium chlorides were taken up in a minimum amount of concentrated hydrochloric acid, and a few drops of a saturated solution of antimony trichloride added to precipitate the caesium as a double chloride of antimony and caesium. The precipitate, if any, was washed with a mixture of hydrochloric acid and antimony trichloride solution and dissolved in 5N hydrochloric acid. The antimony was eliminated as sulphide and the filtrate evaporated to dryness, giving caesium chloride. The weight of caesium chloride was deducted from mixed chlorides of rubidium and caesium to obtain the amount of rubidium chloride. If no caesium was found on the addition of antimony trichloride, the percentage of rubidium present was calculated from the weight of rubidium chloroplatinate. A distinct precipitate was obtained with antimony trichloride when caesium was present in an amount equal to .0003 gm. Cs<sub>2</sub>O.

## METHOD FOR THALLIUM.

Two grammes of mica were heated with sulphuric and hydrofluoric acid and fumed till all HF was removed. After diluting with water the solution was partly neutralised with sodium carbonate, and the thallium reduced to the thalious state with sodium sulphite. Sodium carbonate was then added in excess and after warming for some time the precipitate, consisting mainly of aluminium hydroxide, was filtered off and washed. To the filtrate ammonium sulphide was added to precipitate the thallium. In each sample tested a very small black precipitate was formed. This was tested for thallium by dissolving in dilute sulphuric acid, and after boiling off  $H_2S$ , nearly neutralising with sodium carbonate. The cold solution was saturated with sulphur dioxide and treated with potassium iodide. If thallium be present in appreciable amounts a yellow precipitate of thallium iodide should be obtained. No precipitate of thallium iodide was obtained from any of the micas examined, but on testing the solution the characteristic thallium line was observed by means of the spectroscope.

In only one case, the biaxial lepidolite from Tabba, was a weighable amount of caesium recovered, but in all the other micas tested, although no precipitation took place on the addition of antimony trichloride, caesium could be detected spectroscopically in the solution.

Details of the methods employed in the spectroscopic examination of the micas were as follows:—

For the qualitative detection of rubidium and caesium by the spectroscope.

The alkali chlorides were prepared by the Lawrence Smith method from 0.5 gram mica. The dry chlorides were extracted with a few drops of conc. hydrochloric acid and 90 per cent. alcohol. This dissolved most of the rare alkalis along with sodium and potassium chloride. The solution was evaporated to dryness and the lithium removed from the dry residue by two extractions with a mixture of 5 ccs. absolute alcohol and 5 ccs. anhydrous ether, and decanted through a filter wet with ether alcohol mixture. The decantations were continued until a spectroscopic examination of the filtrate showed it to be lithium free. The filter paper was allowed to dry and the residue washed into the dish containing the alkali chlorides and the contents evaporated to dryness, dissolved in a small portion of water and chloroplatinic acid added. The precipitated rubidium, caesium and potassium chloroplatinates were filtered and washed repeatedly with hot water to remove the more soluble potassium chloroplatinate. Rubidium and caesium chloroplatinates were revealed by spectroscopic examination of the wash water from the mixed chloroplatinates. The minimum quantity of hot water should be used at this operation. The rubidium and caesium chloroplatinates remaining after washing with hot water were washed by decantation into a platinum boat and the double salts decomposed by gentle heating in a stream of dry hydrogen. The rubidium and caesium chloroplatinates were thus reconverted into their respective chlorides and platinum deposited. The mixed chlorides in the boat were dissolved in two drops of water and the solution examined with the spectroscope.

It was found necessary to remain in the dark room about twenty minutes before making observations with the spectroscope. A non-luminous flame about  $\frac{1}{2}$  inch long from a small burner was found most satisfactory for the

production of the spectrum. The lines observed were—for rubidium two lines in the violet of wave length 4215·6 and 4201·8, and for caesium two lines in the violet end of the spectrum of wave length 4593·2 and 4555·3. To obtain a permanent record of rubidium and caesium in the mica from Londonderry by means of a spectrogram two grams of mica were taken and treated in exactly the same way as for the preparation of the chlorides of rubidium and caesium for visual spectroscopic observations. The carbon arc was used for exciting the spectra. The carbon rods used for the arc were first found to be free from rubidium and caesium. Before placing the rubidium and caesium chlorides on the carbon arc the spectrograph was adjusted and the plate placed into position. The poles of the carbon arc were then moistened with the solution of rubidium and caesium chlorides obtained from the mica and the exposure made. On the same plate exposures were made, using pure salts of rubidium and caesium chlorides, and their lines so recorded served as standard lines for reference. Lines for rubidium and caesium obtained from the alkalis and from the mica coincided with those from the pure salts. This conformed the presence of rubidium and caesium in the biaxial mica from Londonderry.

The following method was adopted for the detection of thallium by the spectroscope.

One gram of mica was decomposed with conc. sulphuric and hydrofluoric acids, evaporated nearly to dryness and the mass taken up with about 5 ccs. of water, filtered, and the filtrate just neutralised with sodium carbonate. The filtrate was made up to 50 ccs. and saturated with hydrogen sulphide, allowed to stand overnight and decanted as much as possible through a filter from the brownish black precipitate which might contain thalious sulphide. A trace of the black precipitate was placed on a platinum wire and the spectrum line for thallium observed in a small non-luminous flame placed in front of the adjusted spectroscope.

The most distinctive and intense line is one of wave length 5350·5 in the green end of the spectrum. A blank was conducted with all re-agents used throughout the examination with a negative result.

To obtain a permanent record of thallium in the mica from Londonderry, two grams of mica were taken and treated by the method given for the qualitative spectrum examination for thallium on the visual instrument. Again the carbon arc was used for exciting the spectra, and a solution of thallium nitrate used to give a standard spectrum for reference to the spectrum obtained from the mica. Both exposures were made on the same plate and so the spectra were easy to compare. This plate confirmed the presence of thallium in the biaxial mica from Grosmont Mica Mine, Londonderry.